REMOVAL OF ACRYLIC ACID FROM PROCESS WATER USING CONTINUOUS ADSORPTION

AIRINA BINTI ZUBIR

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Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Adsorption processes have been widely applied in chemical industry for water treatment, valuable compound recovery and undesired compound removal. Continuous adsorption using fixed bed adsorption column has shown its big roles in the large scale of industry. This research aims to study the acrylic acid removal from industrial process water by using continuous adsorption system. Three series of adsorption columns using coconut shell based activated carbon as adsorbent are employed in this study. The process water containing 4% acrylic acid was fed to the column. The adsorption removal efficiency for different feed flow rate through the column and different amount of the adsorbent were studied. The result shows the composition profile concentration of acrylic acid in the outlet flow of each column as a function of time. Therefore, this concludes that continuous adsorption of acrylic acid waste is favorably influenced by a feed flow rate and the weight of adsorbent. The improvement research study was proposed which it should test with high number of continuous column also increase height of bed with regeneration facility because the concentration is too high and the economic analysis can be carried out.

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LIST OF SYMBOLS

Pb	Lead
H_2S	Hydrogen Sulfide
C_t	Concentration at times
C_0	Initial concentration
C_{eff}	Concentration Effluent
V_1	Volume 1
V_2	Volume 2
g	Gram
L	Liter
°C	Degree Celsius
ppm	Part per millions
µ	Micro
n	Nano
m	Meter
%	percent

LIST OF ABBREVIATIONS

AA	Acrylic Acid
AC	Activated Carbon
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
HPLC	High Performance Liquid Chromatography
NOM	Natural Organic Compound
TFA	Trifluoroacetic Acid
USA	United States of America
VOC	Volatile Organic Compound

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Adsorption process of a compound involves accumulation at the interface between two phases which are liquid-solid or a gas-solid. The molecule that accumulates, or adsorbs, at the interface is called an adsorbate, and the solid on which adsorption occurs is the adsorbent. Adsorbents of in water treatment include activated carbon; ion exchange resins; adsorbent resins; metal oxides, hydroxides, and carbonates; activated alumina; clays; and other solids that are suspended in or in contact with water.

Acrylic acid organic compound is generally not persistent in the environment because of its reactivity. In biochemical oxygen demand (BOD) studies, acrylic acid has been shown to degrade 81% in 22 days in water inoculated with sewage seed. Acrylic acid is also amenable to anaerobic treatment, degrading to about 75% of theoretical methane in acclimated cultures. Acrylic acid is moderately toxic to aquatic life, but not persistent in aquatic environments, due to rapid oxidation. Large releases can deplete dissolved oxygen.

Acrylic acid released to the atmosphere will react with ozone and photochemically produce hydroxyl radicals, resulting in a half-life of six to fourteen hours. Since acrylic acid is miscible with water, it would not be expected to absorb significantly on soil or sediment.

The activated carbons from artificial materials have high surface area and extensive chemistry for the continuous adsorption. Nowadays, activated carbons are widely used in a large range of applications, such as medical uses, removal of pollutants and odors and gas purification. Activated carbons are used worldwide in a great many industrial separation processes because of their ability to preferentially adsorb particular chemicals when introduced to solutions containing those chemicals (Mozammel *et.al*, 2002).

1.2 Problem Statement

Acrylic acid present in waste water 4% along with other components. Based on the data given on the BASF PETRONAS Chemicals process water, there are 23 others component that dilute in this water which this amount is not including acrylic acid. In this process water, the composition of water is approximately 87 weight percentage (wt %) and AA has the highest amount which is 4 wt%. Then, this amount is followed by acetic acid, formaldehyde, maleic acid anhydride with the value approximately about 3.3 wt%, 2.3 wt% and 1.8 wt% respectively. The current technology is incinerating the process water in the boiler and converts the organic components in to carbon-di-oxide and steam which consumes large amount of energy. So this research aims to remove acrylic acid from industrial process water by using continuous adsorption system because the concentration is too high.

1.3 Objectives

To develop continuous adsorption system to remove acrylic acid from process water

1.4 Scope of Research

The scope of this research is to identify the optimum conditions of the effluent concentration for continuous column of the removal of acrylic acid aqueous solution must be varied. The equilibrium between acrylic acid organic compound in the solution and the adsorbent surface is practically research using continuous adsorption.

1.5 Rationale & Significance

Rationale. The objective of the present study is to stimulate adsorption process for the organic compound using fixed-bed continuous adsorption column. Laboratory experiments have been proving that the granular activated carbon as adsorbent to remove organic compound. In this research, the results obtained from the experiments studies on continuous adsorption system can be used to replicate in wastewater treatment.

Significance. Adsorptive of acrylic acid (AA) has been found to be very efficient because exposure to AA can occur through all the three dermal, inhalation and ingestion routes. From the studies on the continuous adsorption, the results can be used to relate the adsorption organic compound with activated carbon using fixed-bed continuous adsorption column.

CHAPTER 2

LITERATURE REVIEW

2.1 Acrylic Acid Organic Compound

Acrylic acid (AA) is an unsaturated organic acid and is very toxic to living species. Exposure to AA can occur through all the three dermal, inhalation and ingestion routes. The fumes of AA have an acrid and unpleasant odor. AA imparts toxicity to water and is highly injurious to aquatic organisms. It severely irritates the skin, eyes, respiratory system and the gastro-intestinal tract of humans. The hazardous property of acrylic acid has been presented elsewhere.

AA is widely used in a variety of industrial processes, e.g., paints, synthetic fibers, adhesives, papers and detergents. It is released to environment during the manufacture of acrylic ester, water soluble resin and flocculants. In a typical acrylic manufacturing unit, the wastewater has AA concentration in the range of 10–20 g/l along with several other toxicants of AA family, namely, acrylonitrile, acetonitrile, etc. Such wastewaters also have very high concentration of dissolved solids, turbidity, very high chemical oxygen demand (COD), high alkalinity and many heavy metals. Therefore, adsorptive treatment of AA bearing wastewaters has been found to be very efficient (Kumar *et.al*, 2010).

Due to the breakdown of acrylic acid in the environment and its moderate acute toxicity, the chemical would not be expected to be toxic to aquatic or terrestrial animals at levels normally found in the environment. As a volatile organic compound (VOC), acrylic acid can contribute to the formation of photo-chemical smog in the presence of other precursors. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute (short term) effects are seen two to four days after animals or plants come in contact with a toxic chemical substance.

Acrylic acid has slight acute toxicity to aquatic life and high toxicity to birds. Insufficient data are available to evaluate or predict the short-term effects of acrylic acid to plants or land animals. Chronic toxic (long term) effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Chronic effects can be seen long after first exposures to a toxic chemical. Because of water solubility and vapour pressure most (about 90%) acrylic acid released to the environment is expected to end up in water.

The chemical can be removed from the atmosphere in rain. If released to soil the chemical leaches into groundwater or surface waters. Leaching into ground or surface waters is the major route of removal of acrylic acid from soils due to the chemical's high water solubility and low vapour pressure. Bioaccumulation of acrylic acid is not expected to be significant. Acrylic acid exists in the atmosphere in the gas phase. The dominant atmospheric loss process for acrylic acid is by reaction with the hydroxyl radical. Based on this reaction, the atmospheric life is only expected to be a few days. In the air acrylic acid reacts with ozone to produces glyoxylic acid and formic acid. Wet and dry deposition of gaseous acrylic acid may also be important. Acrylic Acid is biodegradable. It is also destroyed by sunlight in surface soils and water. It is slightly persistent in water but will degrade within a few weeks or months.

2.2 Applicability of Activated Carbon (AC)

AC is dominantly used for purposes of adsorption, a task for which it is well designed. Essentially, adsorption is restricted to working in one of two phases, from the gas/vapor phase (usually air) or from the liquid phase (usually water). Fortunately, there is only one gas/vapor phase, but for liquids, two distinct phases need to be considered, namely adsorption from aqueous systems and adsorption from non-aqueous systems. Adsorption from solution, in comparison, is relatively simple to do experimentally, as no volume changes are involved and modern analytical techniques can be easily adapted to measure concentration changes in solutions.

Competitive adsorption may occur between the solvent and the solute. Adsorption from solution may be further complicated because the solute may change chemically, or its concentration may change in the solution. Thus, concentration of an acidic molecule is a function of the pH of the solution and it is to be noted that both the non-dissociated molecule and an associated ion may be adsorbed. It is impossible to describe adequately the large number of liquid-phase applications allocated to AC. The following list below indicates the wide-ranging scenarios for AC (Marsh and Rodriguez-Reinoso, 2006):

a) Drinking water availability, to improve taste, smell and color including removal of chlorinated compounds and other Volatile Organic Compound (VOC).
b) Improvements to ground water purity, contaminants coming from disused sites of heavy industries.
c) Treatments of both industrial and municipal wastewater.
d) Mining operations require feed water treatment, metallic ion adsorption (gold and other metals), adsorption of excess flotation reagents and adsorption of Natural Organic Material (NOM).
e) Pharmaceutical processes, including purification of process water

f) The food, beverage and oil industries for removal of small, color and unacceptable tastes.

g) The electroplating industries require purification of wastewaters containing Pb, Cr, etc.

Figure 2.1: Granular Activated Carbon form

The application of AC in water treatment is mainly centered in the removal of pollutant organic compounds. These compounds can be classified in three different categories: (1) NOM, (2) synthetic organic compounds and (3) by-products of chemical water treatment. The removal of water contaminants by active carbon is the major market (55% in the USA) for liquid-phase applications which 80% of total AC demands in the USA. Of the total US water treatment market, about 50% is in drinking water, 40% in wastewater and the rest in ground water markets. Both powdered and GAC are used in the water treatment, the tendency being toward use of the granular type because of its regeneration capability (Marsh and Rodriguez-Reinoso, 2006).

When the powdered form of AC is used, it is added to the slurry with automatic feeders. Dosage rates of AC in taste and odor control depend on the type of carbon and the level of impurities in the water, but in general terms the dosage is low, and the carbon can last for up to one year. As a result, it is not usually economic to regenerate the carbon, and spent carbon is generally discarded. Granular Activated Carbon (GAC) is preferred when there is a persistent problem with taste and odor control, and it is also used in special filters and disposable cartridges in industrial, commercial and residential installations.

GAC is used in gravity columns, through which water flows continuously for a set contact time. Contacting systems can be of the up-flow or down-flow type, the former adsorbing organic compounds, whereas the latter filters suspended solids in addition. In an up-flow system, replacement of the spent carbon is carried out from the bottom of the column, with addition of new carbon at the top, while the unit remains in operation. In a down-flow system that does not have pre-filtration, suspended solids may accumulate at the top of bed, requiring periodic back-washing of the bed to relieve the pressure drop caused by the accumulated solids. This type of bed is operated in series or in parallel. As the carbon will be exhausted first at the top of the bed, it is necessary to remove the entire bed in order to replace the carbon. The world's largest municipal GAC potable water treatment system was installed in Cincinnati, Ohio 1989 with a potential capacity of over 830 million liters per day (Marsh and Rodriguez-Reinoso, 2006).

Wastewater is treated involves the removal of inorganic and organic compounds by adsorption. It results in an extremely high-purity effluent, where the BOD can be reduced by over 99%, to 1 mg/L. AC is used in the treatment of industrial wastewater to upgrade the water for reuse or to pre-treat effluents prior to discharge into municipal treatment plants, rivers and streams. Adsorption by an AC may be used as the only treatment before biological treatment or as a tertiary process after biological treatment (Marsh and Rodriguez-Reinoso, 2006)

AC is used to purify industrial wastewater, as it removes not only biodegradable organic compounds, but also chemicals that are not responsive to, or are toxic to, conventional biological treatments. These include pesticides, phenols, organic dyes and polyols. AC is used to treat effluent wastes from chemical factories, rubber tread factories, fabric dyeing, fertilizer plants, pulp, and paper mills, etc. AC systems are more flexible than biological ones as they can handle sudden fluctuations in the concentration of impurities, and the water purity can be controlled to meet specific requirements (Marsh and Rodriguez-Reinoso, 2006).

The selection of the AC for a given application (solutes to be retained, concentration, stream flow, etc.) is made by dynamic tests in pilot adsorption units. The determination of the adsorption isotherm of a given solute over a wide range of concentration is the method to obtain the equilibrium capacity of the adsorbent. In this way, the amount of solute it can remove from the solution can be estimated and consequently the suitability of the AC for achieving the required removal of the solute (Marsh and Rodriguez-Reinoso, 2006).

The analysis of the adsorption isotherm gives the adsorption capacity at equilibrium, but it says nothing about the time required reaching equilibrium, and this is a very important parameter in the design of an adsorbed bed. Once a group of carbons has been selected, it is necessary to carry out dynamic tests to determine the breakthrough curve to determine the volume of water that can be treated by the carbon bed before it become saturated, or before the concentration of the solute in the effluent (at the exit of the adsorbent bed) become higher than that required (breakthrough point). The breakthrough curve in an adsorption system depends on several parameters. It depends on the space velocity of the stream (the ratio between the volumetric flow and the volume of the bed); it is clear that the adsorbent bed can be used for a larger period of time with low space velocities.

But, the breakthrough curve also depends on the characteristics of the stream to be treated (composition, concentration of impurities, temperature, pH) and on the adsorbent (surface characteristics, particle size). After the AC becomes saturated, it is sometimes necessary to regenerate it in order to recover its adsorption capacity. Physical adsorption is a reversible process, and desorption can be more or less easily achieved. Regeneration is usually carried out by means of a thermal process. The exhausted carbon is taken off the adsorption column as slurry. It is dewatered and passed to a rotary kiln, where it is heat treated under controlled conditions and with a limited oxygen content to avoid carbon combustion. This treatment removes residual water and volatilizes organic compounds, which are also oxidized. Then the carbon is quenched with water, washed and recycled. The carbon is regenerated either on or off site. Some carbon losses (2-10wt %) is unavoidable during the regeneration step, and fresh carbon has to be supplied. The regeneration process takes about 30min (Marsh and Rodriguez-Reinoso, 2006).

2.3 Coconut Shell Based Activated Carbon

A coconut shell-based activated carbon was studied as hydrogen sulfide adsorbent in four subsequent adsorption/ regeneration cycles. The regeneration of exhausted carbon was done using washing with cold and hot water with a defined ratio of water volume to the unit weight of carbon. The observed changes in the capacity were linked to such surface features of activated carbons as pH and porosity. The cold and hot water washing result in the similar capacity for H_2S adsorption. After the first adsorption run, the capacity of carbon for hydrogen sulfide adsorption significantly decreased (around 60%). The subsequent runs revealed more or less constant capacity with similar efficiency for the removal of sulfur species (Bagreev *et.al*, 2000).

The results indicate that after the first run the most active adsorption cites located in small pores are exhausted irreversibly. The sulfur adsorbed on those sites is strongly bound as elemental sulfur and sulfuric acid. Despite this, the carbon surface was found to have other adsorption/oxidation sites which can be regenerated using cold or hot water washing. Besides sulfuric acid being removed from the pore volume of activated carbon a significant percentage of elemental sulfur was also removed (Bagreev *et.al*, 2000).

Activated carbon can be produced from different raw carbon resources like lignite, peat, coal, and biomass resources such as wood, sawdust, bagasse, and coconut shells (Ioannidou and Zabaniotou, 2006). However, the abundant supply of coconut shell as a waste-product from the coconut oil and desiccated coconut industry makes production of activated carbon from this material more financially viable since using grain or coal as raw materials for activated carbon will require manufacturers extra amount of money for procurement. Furthermore, besides being an amorphous form of carbon that can absorb many gases, vapors, and colloidal solids, coconut shell activated carbons are advantageous over carbons made from other materials because of its high density, high purity, and virtually dust-free nature. These carbons are harder and more resistant to attrition (Gratuito *et.al*, 2008).

Figure 2.2: Coconut Shell Activated Carbon

2.4 Fixed-Bed Adsorption Column Studies

In the studies of fixed-bed adsorption processes, breakthrough and number of bed volumes are normally used in the description and comparison. The breakthrough is usually defined as the phenomenon when the effluent concentration from the column is about 3–5% of the influent concentration (Chen *et.al*, 2003).

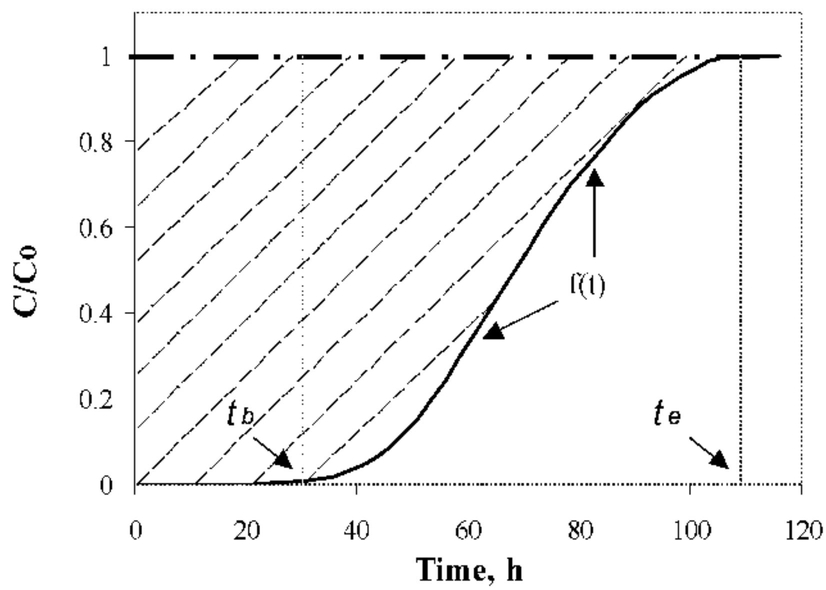

Figure 2.3: Typical Breakthrough Curve of Carbon Fixed-Bed Column (Chen *et.al*, 2003)

Fixed-bed adsorption process has been widely used to remove many organic pollutants from industrial wastewater, and the relevant breakthrough curves for a specific adsorption process are essential when determining the operating parameters such as feed flow rate. Although many models were developed to predict the breakthrough curve, most of them are sophisticated and need many parameters determined by serial independent batch kinetic tests or estimated by suitable correlations (Pan *et.al*, 2005).

The performance of a fixed-bed column is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The loading behavior of the adsorbed solution in a fixed-bed is usually expressed in term of C_t /C_0 as a function of time or volume of the effluent for a given bed height, giving a breakthrough curve (Han *et.al*, 2009).

Fixed bed adsorber columns have been widely used for treatment of textile industry effluents. In this regard, one important aspect to consider will be the analysis of the columns performance subjected to different operating conditions. Also, the design of the adsorption columns usually requires information from pilot-plant experiments. However, a mathematical model, once it has been validated, can minimize the number of experiments associated with new operating conditions, and therefore decrease additional costs. A valid model can predict the system dynamics expressed through breakthrough curves with respect to adsorption equilibrium isotherms (Goshadrou and Moheb, 2011).

2.5 Continuous Adsorption Systems

The adsorption systems related to granular activated carbon (GAC) contactors. It can be classified by the following characteristics: (1) driving force-gravity versus pressure; (2) flow direction-downflow versus upflow; (3) configuration-parallel versus series; and (4) position-filter-adsorber versus postfilter-adsorber. GAC may be used in pressure or gravity contactors. Pressure filters enclose the GAC and can be operated over a wide range of flow rates because of the wide variations in pressure drop that can